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ORGANIC CONTAMINANTS IN GROUNDWATERS AT SEVERAL
ONTARIO LANDFILLS

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ABSTRACT

The occurrence and migration of contaminants in groundwater impacted by leachate at six municipal landfill sites are being studied to determine the hydrogeological, geochemical, and microbiological influences on their mobility and persistence. Of special interest are processes of attenuation (sorption, biodegradation) and dilution (hydrodynamic dispersion). Currently, studies are underway in sandy aquifers (CFB Borden, North Bay and Woolwich), less permeable sandy silty glacial till (CFB Borden), and in fractured shale and dolomite (Burlington and Hamilton). Studies at a landfill site on fractured clay-till in southwestern Ontario will begin in 1985.

At the North Bay site, where landfilling began in 1962, organic contaminants are found throughout the 1 km sandy aquifer. Chlorinated solvents are restricted to the immediate vicinity of the landfill, probably because of anaerobic biodegradation. Aromatic hydrocarbons may also be degraded in the final 300 m section. At the Woolwich site, the chlorinated solvents are migrating further while aromatic hydrocarbons are only found in low concentration even near the landfill. Aerobic conditions appear to dominate here, resulting in persistence of chlorinated methanes and ethanes and degradation of aromatics. Additional research into the hydrogeological controls of contaminant migration at these sites is underway.

At the landfill on sandy silty glacial till at Canadian Forces Base Borden, where landfilling began in 1976, a plume of groundwater contamination has developed that is readily mappable over a distance of 150 m based on chloride and total dissolved organic carbon. Detailed studies of the organic compounds in this plume will soon be initiated.

Contamination of a fractured bedrock system at the Hamilton site by organics has been difficult to define because the major contaminants are aliphatic and aromatic hydrocarbons which also occur naturally in these sedimentary bedrock strata. Therefore, research into the occurrence of hydrocarbons and S-bearing heterocyclic hydrocarbons in uncontaminated groundwaters is underway in order to identify better "leachate indicator" parameters.

At a landfill on fractured shale in Burlington, normal inorganic indicators of leachate contamination did not provide a basis for delineating the zone of contamination. At this site 1,1,1 trichloroethane, chlorobenzene and paradichlorobenzene at very low concentrations have been used to trace the zone of landfill impact for a considerable distance from the landfill.

INTRODUCTION

It has long been recognized that municipal landfills in Ontario and elsewhere in humid or semi-humid climatic regions produce leachate that causes contamination of groundwater. Zones of contaminated groundwater, referred to as leachate plumes, are commonly extensive at landfills situated on permeable, geological materials. The hydrogeology group at the University of Waterloo began investigations of the extent and chemical nature of leachate plumes in Ontario in 1976. Until recently these investigations focused on the inorganic contaminants in unconfined sand aquifers. The results of these inorganic studies are presented by Cherry (1982), Cherry (1983), and Cherry et al. (1981). In the past three years our landfill investigations have been extended to include landfills on other types of geological materials and to include organic contaminants. The investigations of organic contaminants are being undertaken in collaboration with the Environmental Engineering Group at Stanford University and with the Department of Environmental Chemistry and Biology at the Oregon Graduate Center.

Six landfills in Ontario are currently being investigated as part of this long-term research program. Three of the landfills are situated on unconfined sand aquifers. One of these landfills, referred to in this paper as the old Borden landfill, is located at Canadian Forces Base Borden near Alliston. The other two landfills are near the City of North Bay and in Woolwich Township near Elmira. The landfills at these three sites are about 20 years old and the aquifers are quite permeable so that there has been an opportunity for relatively large plumes of leachate contamination to develop. The fourth landfill is also situated at Canadian Forces Base Borden. This landfill, referred to as the new Borden landfill, began operation in 1976. It is situated on a deposit of sandy silty glacial till. Because this landfill is young and because the geological material is only moderately permeable, there has been much less opportunity for a zone of groundwater contamination to develop at this site than at the other landfill sites included in this investigation.

The other two landfills are situated on fractured bedrock. One is located on the lower part of the Niagara Escarpment in Burlington about 3.5 kilometres from Lake Ontario. This landfill, referred to as the Bayview Park landfill, is situated on less permeable fractured shale. The other landfill is located on the upper part of the Niagara Escarpment in Hamilton, about 5 km from Lake Ontario. It is situated on moderately permeable dolomite which is underlain by slightly permeable shale. This landfill is known as the Upper Ottawa Street Landfill. Landfilling began at these two sites between 20 and 30 years ago.

The old Borden landfill, the Bayview Park landfill and the Upper Ottawa Street landfill are no longer in use. They have received a final cover of earth material and the surfaces have been planted to grass. The other three landfills are continuing to receive refuse.

The purpose of our current investigations at each of these landfills is to determine the nature of the inorganic and organic contamination within the contaminant plumes and to determine the distributions of selected organic contaminants and the processes that control these distributions. With the support of the Ontario Lottery Fund, our investigations of most of the above-mentioned landfills will continue for another two years. This paper is a brief report on the nature of our studies. In addition to the landfills mentioned above, our investigations in the next two years

will include a landfill situated on clayey glacial till of very low permeability in southwestern Ontario, where contaminant migration is expected to be governed by molecular diffusion rather than by groundwater flow. A search for an appropriate study site is near completion and field studies will begin at the selected site in the spring of 1985.

In this paper two of the six landfills, the new Borden landfill and the Upper Ottawa Street landfill, are mentioned only briefly.

METHODS OF INVESTIGATION

Prior to our investigations, a hydrogeological study of each site had been conducted by consulting firms as part of the normal investigative activities that are usually undertaken by regional governments or landfill operators. This information was used by us in the design of our research programs, and as a basis for the installation of a network of groundwater monitoring devices to supplement the monitoring piezometers that were already in place at each of the sites.

At five of the study sites, monitoring networks consist primarily of multilevel monitoring devices constructed of small diameter polypropylene sampling tubes. At the three landfills on sand aquifers multilevel monitoring is provided by bundle piezometers (Figure 1). Bundle piezometers contain eight or nine individual piezometers, each extending to a different depth, to provide vertical profiles of hydraulic head and water chemistry. No seals are used between the piezometer tips because in cohesionless sand aquifers, the sand caves in rapidly and apparently quite tightly around the tubes.

The bundle piezometers were installed using hollow stem augers. Their design and use are described in detail by Cherry et al. (1983). The bundle piezometer was developed as a monitoring device for use in investigations of landfill plumes in sand aquifers by experimentation at the old Borden landfill and then in later years it was applied at the Woolwich and North Bay sites.

The main advantage of the use of bundle piezometers at these sites is that vertical profiles of water chemistry are obtainable from a single borehole. Comparable profiles using conventional piezometers require many more boreholes. At sites where the water table is deep, the efficiency of bundle piezometers is less than at shallow water table sites because water sampling is much more time-consuming. This was a significant problem at the Woolwich site where the depth to the water table below ground surface ranges from 10 to 20 metres. To alleviate this problem, a narrow diameter sampling pump was developed by Robin et al. (1982) for use at this site. This pump is now manufactured and marketed by an Ontario company (Solinst, Burlington).

The monitoring networks at the two sites on fractured bedrock consist of conventional piezometers installed previously by consultants and multilevel monitoring devices (Figure 2). The multilevel monitoring devices consist of a bundle piezometer within a PVC casing. Each piezometer tube is connected to a sampling part in the casing. The segments of borehole sampled by each tube are isolated from above and below by an inflated packer. The packers are constructed of a chemical

sealant (Dowell sealant), which expands when contacted by water, which is pumped into the PVC casing. It contacts the chemical sealant through holes in the PVC casing adjacent to the packer. A rubber membrane covers each packer to prevent contact with groundwater surrounding the monitoring device.

The number of piezometers that can be placed in each multilevel device depends on the size of borehole. The boreholes used at the Upper Ottawa Street Landfill Site in Hamilton were approximately 7 centimeters in diameter. Each multilevel device contained between 5 and 7 piezometers. At the Bayview Park site in Burlington, the boreholes were approximately 10 centimeters in diameter so that multilevel devices contained between 10 and 12 piezometers. Because the cost of drilling boreholes in rock is high, there is a strong financial incentive to place as many piezometers as possible in each borehole. The disadvantage of these multilevel devices is that assembling is more difficult and time-consuming than is the case for larger diameter conventional piezometers.

The multilevel device for bedrock was originally developed for use at the Upper Ottawa Street landfill and later used at the Bayview Park site in Burlington. Details regarding the design and construction of the device are provided by Cherry and Johnson (1982), and by Cherry et al. (1985). The pump used for drawing water samples from the multilevel devices at the fractured rock sites is the one mentioned above for sampling bundle piezometers in deep water table areas (Robin et al. 1982).

At the new Borden landfill, conventional piezometers are used for groundwater monitoring. The silty till at this site does not provide the sediment caving characteristics of cohesionless sand which are necessary for the use of bundle piezometers. Nor, does it provide smooth open boreholes of the type encountered in bedrock. Smooth open holes are necessary for the Dowell-sealant type multilevel monitoring devices. Therefore, conventional piezometers were used at this site.

The network of conventional piezometers that existed prior to our investigations has been augmented to provide more detailed monitoring. Nests of conventional piezometers are used to provide vertical profiles of water chemistry. In general, only one piezometer is installed in each borehole, the tip surrounded by a sand pack and sealed from the rest of the borehole in the bentonite.

The monitoring network that currently exists at each of the landfill study sites was installed in phases. A limited number of monitoring devices were installed in each phase, from which data were acquired and used as a basis for the installation of additional devices. The least number of monitoring sites exists at the Bayview Park landfill site where there are 33 conventional piezometers and five multilevel monitoring devices. The most monitoring devices exist at the old Borden landfill where there are approximately 69 conventional piezometers and 75 multilevel devices.

Water samples from nearly all of the monitoring devices at each of the landfill sites have been analysed for chloride and electrical conductance. Many of the samples have also been analysed for total dissolved organic carbon (DOC). A lesser number of samples from each site have been analysed for a large suite of inorganic constituents such as major ions and trace elements.

Trace organic compounds in selected samples from each of the sites, except for the new Borden landfill, have been analysed by gas chromatography and mass spectrometry. Although many organic compounds have been identified in the plumes, these methods provide identifications of compounds that constitute only a few percent of the total mass of dissolved organic compound in any of the samples. The sampling and analytical methods used in the investigations of organics at the Borden, Woolwich and North Bay sites are described by Reinhard et al. (1984) and the sampling and analytical methods used in the investigation of the Bayview Park landfill site are described by Pankow et al. (1984).

In addition to water sampling, the networks of monitoring devices at each of the landfill sites are used for water-level monitoring and for performing field tests for hydraulic conductivity. The water level and hydraulic conductivity data enable interpretations of the groundwater flow patterns and flow rates to be developed for each site.

One of the objectives of these investigations is to compare the positions and shapes of the leachate plumes determined from chemical analyses of the water samples to the positions and shapes that one would predict on the basis of information pertaining to hydraulic conductivity, water-table configuration and the distribution of hydraulic head. At some of the sites, mathematical models are being used to develop more formal predictions based on these types of data. The most recent application of a mathematical model for simulation of contaminant migration is described by Hokkanen (1984) who successfully simulated in considerable detail the 40 year development of the plume at the old Borden landfill.

RESULTS AND DISCUSSION

Plumes Delineated by Chloride and DOC

At the three landfill sites on sand aquifers and at the landfill on sandy, silty glacial till, plumes of leachate contamination were easily delineated using chloride and DOC.

The plume at the Borden landfill is the longest and widest, extending approximately 900 to 1,000 metres northward from the edge of the landfill. It is about 700 m wide with a fan-like shape. Landfilling at this site began in 1940 so that more than four decades of contaminant migration have been necessary for the plume to grow to this extent. The plume is thickest beneath the landfill where the bottom of the plume goes as deep as 25 m below the water table. The plume extends nearly to the bottom of the aquifer here because of the effect of a ephemeral water-table mound beneath the refuse and possibly because of an effect of plume density.

The Borden landfill plume becomes much thinner in the direction of groundwater flow, which is northward. The plume becomes thinner because the aquifer becomes thinner in this direction. At its northern extremity, the plume exists in only the lowest 2 or 3 metres of the aquifer. Thus, detailed vertical profiles of Cl or DOC were necessary to identify the plume in this area (MacFarlane et al. 1983). The average northward groundwater velocity in the sand aquifer is about 10 to 20

m/yr in the northern-most part of the plume where the aquifer is thin. The southern half or two-thirds of the plume has a relatively stable shape, whereas the northern part is continuing to expand northward at the groundwater flow rate mentioned above.

The North Bay landfill is situated on unconsolidated glacio-fluvial sands generally 17 m to 25 m thick, underlain by a thin (< 2 ,) zone of less permeable, till and then granitic bedrock. Contaminated groundwater flows southwest from the landfill, under a large sand pit and discharges in springs adjacent to Chippewa Creek, about 700 m to the southwest (Figure 3).

The leachate-contaminated plume has been defined by repeatedly sampling (1981-present) the multilevel piezometers. Figure 3 shows the contours of maximum chloride (Cl) concentration in 1982. Figure 4 shows the Cl concentrations in a vertical profile along the AA' cross section indicated in Figure 3. Whereas the highest Cl concentrations occupy the middle of the unconfined sand aquifer near the landfill site, the high Cl zone plunges to the bottom of the aquifer within about 200 m of the landfill.

The plume that extends from the North Bay landfill does not spread laterally as does the Borden plume (MacFarlane et al., 1983). The laterally-restricted path of the former may be influenced by bedrock-surface control suggested by a bedrock outcrop immediately east of the plume. This is confirmed in part, by recent geophysical surveys by Dr. J. P. Greenhouse of the University of Waterloo. However, permeability variations as well as a "bedrock valley" may be limiting the lateral spreading.

Groundwater velocities range from about 30 to about 150 m/yr with 70 m/yr considered representative of the overall velocity. Thus, leachate has probably been discharging near site AAA since the mid-1970's. A resampling of the piezometer network in June, 1984 found lower maximum chloride concentrations (520 versus 840 mg/L) than in 1981/82 and the maxima occur 50-150 m from the landfill rather than adjacent to the landfill as in 1982 (Figure 3). This displacement of maximum Cl concentrations is consistent with the 70 m/yr groundwater velocity. The decrease in maximum Cl concentration could be a result of dispersion. These results indicate that the input of Cl and, by inference, other species, from the landfill is not constant. We will assume, however, that the ratio of organic contaminants to Cl has been constant over time. This appears reasonable since a good correlation of TOC (total dissolved organic carbon) with Cl is obtained for most sampling points.

The Woolwich landfill differs considerably from the other two landfills on sand aquifers in that the refuse is deposited in pits that are well above the water table. The bottom of the refuse and the water table are separated by 7 to 10 m of partially-saturated sand. The thickness of the sand aquifer beneath the water table is 15 to 20 m. The water table across the site slopes southeastward, which is the direction in which a plume has developed since landfilling at the site began in the mid-1960's.

The plume, delineated using Cl^- and DOC, extends nearly to the bottom of the aquifer beneath the landfill. Although the plume is easily identified near the landfill on the basis of these two parameters, it is much less distinct beyond 300 to

400 m, where Cl^- and DOC values are much lower and are erratic in the vertical profiles. The position of the leading edge of the plume has not been located in detail because of these conditions.

From values of hydraulic conductivity, a southeastward hydraulic gradient and porosity, calculated estimates of the average groundwater velocity are in the range of about 50 to 150 m/yr. The lack of a clear indication of the plume beyond 400 or 500 m from the landfill is therefore puzzling. Investigations that are in progress are designed to shed some light on this situation.

The smallest plume exists at the new landfill at Borden where the front of the plume has only travelled about 150 metres northward from the edge of the landfill. Landfilling at this site began in 1976. Considering that this landfill is young and that the hydraulic conductivity of the till is much less than the conductivity of the sand aquifers, this plume has travelled relatively far. The average rate of travel of the front of the plume is about 20 m, which is not much less than the average travel rates attributed to the three plumes in the sand aquifers. The moderately steep slope of the land surface causes lateral hydraulic gradient at the site to be much larger than at the sand-aquifer sites.

The background concentrations of chloride and DOC at the four sites described above are very low in comparison to the concentrations of these constituents in the landfill leachate at these sites. Chloride and DOC are therefore well suited for defining the extent of leachate impact on the groundwater zones at these sites. Chloride concentrations in the leachate are generally in the range of 200 to 800 mg/L whereas the background concentrations of chloride are generally less than 10 mg/L. Background concentrations of DOC are generally less than 5 mg/L whereas in the leachate the DOC concentrations are generally in the range of 50 to 5000 mg/L.

At the two landfills on fractured bedrock, chloride and DOC did not serve as useful parameters for delineating the full extent of the groundwater zones impacted by the landfill. At the Bayview Park landfill site, which is underlain by fractured Queenston shale, the groundwater in the shale contains high concentrations of chloride derived from shale. This chloride salt is apparently a relic from the seawater that existed when the shale and other sedimentary rocks formed in southern Ontario. The natural DOC in the groundwater in the Queenston shale is generally less than 5 mg/L. The landfill concentrations of DOC are much higher than the background values. However, the flow pattern in the shale is erratic and the landfill concentrations appear to be quite variable and therefore DOC is not as suitable as a leachate indicator as at the sites on the sand and on sandy silty till. DOC at this site enables the leachate-impacted zone close to the landfill to be delineated but it does not serve as a good indicator of the leachate plume in its down-gradient extremity.

At the Upper Ottawa Street landfill, which is underlain by dolomite and by dolomitic shale, the background concentrations of chloride and of DOC are high and therefore at this site both these parameters are limited in their usefulness for plume delineation. This site is similar to the Bayview Park site in that the groundwater flow system is very complex due to the nature of permeability in the fractured rocks.

Trace Organic Compounds In The Plumes

North Bay Landfill

Studies of trace organic occurrence and migration in the North Bay plume have been underway since 1982, and are ongoing, in part, as a cooperative research program with Stanford University. Results have recently been published (Reinhard et al. 1984, 1984a) and so only a few main results are summarized here.

Figure 5 shows the vertical distribution of Cl, DOC (dissolved organic carbon), methane (CH_4) and selected organic contaminants at location G adjacent to the landfill again in 1982 (Figure 5). Whereas maximum concentrations of Cl, DOC and xylenes occur at a depth of 5 to 10 m, maximum concentrations of benzoic acid, various phenols and trichloroethylene (TCEy) occur at a depth of about 17 m. This distribution has been confirmed on at least four occasions since 1982.

The occurrence of TCEy, which in its industrial product form is organic liquid denser than water, exclusively at depth suggests the possibility of a dense organic liquid phase existing beneath this landfill which is being slowly leached by groundwater flowing near the bottom of the aquifer. However, the much higher concentration of "light" organics, benzoic acid, and phenols at the same piezometer do not support this hypothesis. Other explanations for this vertical variation at G include different inputs along the respective flow lines being sampled at G and possible selective biodegradation of organic components in the different geochemical/microbial environments along the flow lines.

(Table 1 presents the concentration of selected organics in the plume sampled in 1982). Although many organic contaminants persist to the discharge springs, the chlorinated methanes, ethanes and ethylenes have not been detected beyond about 200 m from the landfill (Reinhard et al. 1984 and Oct. 1984 sampling). This is unlikely to represent retardation by sorption as more-readily sorbed organics have moved over 700 m. It could represent only recent disposal of these organics, but this is not considered likely given their long-term use as solvents and degreasers. It is more likely that these organics are being microbially transformed during migration (Reinhard et al. 1984, 1984a).

Only methanogenic bacteria have been conclusively shown to transform these chlorinated compounds (Kobayashi and Rittman, 1982). Although methane does emanate from the landfill in groundwater, it is not clear from CH_4 or CH_4/Cl distributions whether methanogenesis is also occurring in the leachate plume beyond piezometer G. King (1983), using the distribution of stable carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) as well as the distribution of carbon between organic (DOC), inorganic (DIC) and methane (CH_4) pools in migrating groundwater, indicates that methanogenesis is occurring at least until piezometer LL (about 400 m from the landfill), but that the final 300 m of flow might be influenced by methane oxidation. Thus an active methanogenic environment is present where the chloroform, 1,1,1-trichloroethane and trichloroethylene are decreasing to less than 0.1 ug/l (ppb) levels, supporting the concept of biotransformation as the attenuation mechanism for these organics.

The indication of more oxidizing conditions in the latter 300 m of the flow system (King 1983) is interesting in view of the apparent biotransformation of some aromatic hydrocarbons between LL and AAA (Figure 3 and Table 1). Compounds such as o,m,p-xylenes, 1,2,4-trimethyl benzene and naphthalene decrease significantly, even with respect to Cl, between LL-9 and AAA-5. These compounds are generally considered degradable only under aerobic conditions. The lack of measurable (< 0.2 mg/L) dissolved oxygen in all seriously impacted groundwaters could indicate that the required aerobic conditions were not met, but could also indicate that the dissolved oxygen entering these waters by dispersion (mixing) was consumed in the transformation of these aromatic hydrocarbons.

Many other groups of organics such as aromatic acids, polynuclear aromatic hydrocarbons, chlorinated benzenes, are present in this plume. It is hoped that continued research will provide information on the environments conducive to their transformation and on the combined physio-chemical and microbial processes influencing their attenuation in sandy aquifers. We view this site as an outstanding natural laboratory in which to assess landfill-derived organic contaminant migration. The natural complexities such as source input variation, and aquifer variability require that conclusions be based on long-term studies with repeated sampling of critical piezometers.

Woolwich Landfill

A total of 110 sampling points from within twenty-one bundle piezometers have been sampled for analysis of volatile organic compounds. From this work various organic compounds in the groundwater zone have been identified. Near the landfill, leachate-impacted groundwater is characterized by low levels of chlorinated volatiles, higher levels of aromatic hydrocarbons and phenolic compounds, and much higher levels of carboxylic acids. These types of compounds are common in sanitary landfill leachate and are derived from the breakdown of organic materials and, in some cases, from disposal of the compound itself.

The two most common and extensive of these compounds are 1,1,1-trichloroethane and trichloroethylene. There are readily identifiable concentrations of these compounds in the vicinity of the landfill, and much lower concentrations at distance southeastward of the landfill. It is possible that concentration levels that are detectable but that are less than about one microgram per litre are artifacts of the monitoring devices rather than actual contamination in the aquifer. It is known that 1,1,1-trichloroethane and trichloroethylene are sometimes derived from the plastics in glues used in such monitoring devices.

It is expected that 1,1,1 trichloroethane and trichloroethylene would exist in the groundwater close to the landfill because these compounds are commonly seen in contaminated groundwater at landfills in North America and Europe. Such compounds are also commonly seen in groundwater where industrial pollution, not related to landfills, occurs. The fact that these two compounds do not exist at high concentrations beyond a distance about 300 m downgradient of the landfill is consistent with the of some significant degree of adsorption in the aquifer, which would cause them to travel less quickly than the flowing groundwater. It is also possible that biodegradation processes cause attenuation of one or both of these compounds in this aquifer.

The limit for 1,1,1 trichloroethane in drinking water suggested recently by the U.S. Environmental Protection Agency is 200 micrograms per litre. The concentration levels in the Woolwich aquifer are very small relative to this value. The suggested limit for trichloroethylene in drinking water provided by the State of New York is 10 micrograms per litre. A few values above this limit occur very near the Woolwich landfill but not at distances from the landfill. To our knowledge, guidelines for these compounds in drinking water have not yet been produced by the Ontario Ministry of the Environment. The closest drinking-water well is about 1 km from the landfill in the direction of groundwater flow. The zone of identifiable aquifer contamination at the present time therefore has not yet moved sufficiently far to cause closure of wells.

The persistence and mobility of organics at the Woolwich site are difficult to define because of the limited sampling up to 1983. The results of sampling during 1984 may provide a better definition of the areal extent of organic contaminants. Consideration of the potential long-term impact of these organics on groundwater quality must await these results.

Borden Landfill

Groundwater from only about 20 sample points in the bundle piezometers at the old Borden landfill were examined for organic contaminants. The general finding was that organic contaminants were not often present at levels much above background. Four volatile compounds were detected: chloroform, carbon tetrachloride, trichloroethylene and tetrachlorethylene. Concentrations never exceeded 4 mg/L (ppb) and were usually less than 1 ug/l. There was no correlation between distribution of TOC or Cl and these organics.

Low concentrations (< 10 ug/l) and irregular distributions of aromatic hydrocarbons (toluene, substituted benzenes) benzothiazole, and fatty acids are consistent with minor leaching of organic matter from the dominantly burned-fill material. Elemental sulphur was often found. Given a pH of about 7 and an equilibrium among sulphur species, this would imply an Eh of about -200 mV which is consistent with estimates by Nicholson et al. (1983) based on SO_4^{2-} - HS^- measurements. Diethyl phthalate was often found, but, as this is a common plasticizer, it probably is a contamination from sampling or piezometer material. Because of the low and irregular organic concentrations, this site was considered to be less suitable than the other landfill sites for additional detailed studies of organic compounds in the plume.

Bayview Park Landfill

Organic nitrogen, phenol and dissolved organic carbon (DOC) were used as indicators of the bulk organic content in groundwater. When these parameters are present at low levels in background groundwater, the high levels contributed by a landfill can be used to trace contaminations. DOC, is commonly used in this way in sand and gravel aquifers where background levels are a few mg/L while those in the plume may be 10's and 100's of mg/L.

At the Bayview Park site, background concentrations of organic nitrogen, phenol and DOC are quite low in comparison to those found in sand and gravel deposits elsewhere in Ontario. At the three background monitoring locations, phenol has a maximum level of 2 mg/L, while DOC values range between 2.5 and 4.0. Organic nitrogen, the difference between total kjeldahl nitrogen and free ammonia, has a maximum background level of 0.3.

These relatively low background concentrations provide a good contrast with concentrations found downgradient of the landfill. Above background levels of all three indicators occur in the shale for several hundred metres showing an overall decrease with distance. Maximum levels in a piezometer beneath the landfill establish the landfill as a major source of dissolved organic compounds.

Organic nitrogen shows the most gradual concentration reduction, with concentrations approaching background levels about 800 m downgradient of the landfill. While the concentration in the refuse is almost an order of magnitude higher than background levels, elsewhere in the shale, concentrations exceed this by only 1 or 2 mg/L.

Phenol and DOC concentrations are much more erratic than organic nitrogen downgradient of the landfill. Within 350 m phenol levels in the most shallow piezometer in each well nest are at or approaching background while levels in the deeper piezometers are at least 50% of the maximum found in the refuse. DOC concentrations within 600 m downgradient of the landfill are distinctly above background levels, with the exception of the deepest piezometer of this maximum distance.

Samples for trace organic analysis at the Bayview Park site were obtained using two down-hole cartridge samplers described by Pankow et al. (1984a, 1984b). Sample cartridges contain Tenax-GC, to which contaminants are adsorbed when the sampler is positioned down the piezometer. The cartridge, rather than water, is then submitted to the laboratory.

The potential influence of natural organic matter on the bulk organic concentration trends necessitated the use of more diagnostic tracers of groundwater contamination. Three trace organic compounds, 1,1,1 trichloroethane (TCA), chlorobenzene (CB) and paradichlorobenzene (PDCB), were identified in groundwater and used in this capacity. As synthetic compounds, the only source of these compounds in groundwater is the landfill, when it is established that the piezometer materials are not a significant source.

The distribution of TCA, CB and PDCB confirmed the vertical movement of landfill-derived contaminants to depths at least as great as the deepest piezometer. These compounds also indicate that there has been migration of landfill-derived contaminants at least as far towards Lake Ontario as the farthest piezometers from the landfill (3.5 km). Thus, the bottom and the front of the plume have not yet been located.

All three trace organic compounds were found as far 350 m downgradient as of the landfill. Beyond this point, CB is not detectable and PDCB concentrations are approaching non-detectable limits. Concentrations of TCA are still at least 0.5 ug/L at a distance of 800 m, however. Although virtually nothing is known about

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the input of the compounds to the groundwater flow system, the distance downgradient to which each occurs appears consistent with their relative biodegradability.

The occurrence of CB and PDCB is coincident with tritiated groundwater, which implies input to the system after 1953. Because no landfill-related contaminants were introduced to groundwater prior to the opening of the landfill in 1961, the occurrence of TCA in non-tritiated groundwater suggests differential loss of these two constituents to the shale. This loss may be due to diffusion to the shale matrix as suggested by a free solution diffusion coefficient for tritium that is a factor of 2.7 larger than a comparable coefficient for organic compounds structurally similar to TCA. Laboratory measurements of the diffusion coefficient for chloride and tritium in the shale are currently in progress.

SUMMARY AND CONCLUSIONS

At each of the six landfills included in this investigation, extensive zones of leachate impacted groundwater have been identified. In each of these zones the vertical variations of concentrations of both inorganic and organic contaminants are large. The use of multilevel monitoring devices to determine vertical profiles of water chemistry has been essential in the task of determining the zones where highest contamination levels exist.

At the landfills on sand aquifers, the vertical concentration profiles of trace organic compounds are, in general, much different than those of chloride and DOC. Delineation using chloride and DOC therefore will not necessarily provide definition of the most important zones of contamination with trace organic compounds. The lateral distribution of trace organic compounds in the sand aquifers indicate that the absorptive capacity of these aquifers is too low to prevent considerable migration of many hydrocarbons. The solid phase organic carbon content of the sand aquifers are very low and therefore the sand provides little tenancy for absorption of organic compounds.

Distribution of trace organic compounds at the Woolwich and North Bay landfill sites is much more complex than that of the inorganic parameters such as chloride and dissolved organic carbon. This suggests that much more extensive monitoring would be required to provide a basis for predicting the future migration of trace organic compounds relative to the monitoring detail required for inorganic contaminants.

By far the greatest difficulty in delineating zones of leachate migration in the groundwater zone was encountered at the two landfill sites on fractured bedrock. At these sites the pattern of groundwater flow is very complex because the fracture network is complex. The background water chemistry also provided complexities because of high salt concentrations and more variable and abundant concentrations of natural organic carbon. At the landfill site on the Queenston shale it was necessary to use trace halogenated hydrocarbons for identifying the main extent of the zone of leachate-impacted groundwater. At the landfill site on dolomite and dolomitic shale a large number of inorganic and organic constituents were necessary to provide indications of leachate contamination.

Our studies at the six landfill sites indicate that when landfills are situated on moderately permeable or very permeable overburden deposits or on fractured bedrock, extensive zones of leachate-impacted groundwater can develop. In fractured shale, extensive zones of contamination can develop even though the shale has a low permeability. The potential of landfill leachate to cause groundwater contamination does not seem to diminish with landfill age. Thus it is reasonable to expect that the extent of the contaminant zones will gradually increase in future decades and maybe even in future centuries. Although many inorganic contaminants are present throughout leachate plumes, inorganic contaminants that are hazardous in drinking water are rarely observed anywhere but very close to the landfills. Trace organic contaminants pose the main threat to drinking water supplies. Fortunately, of the six landfills that we are investigating, only one is situated in an aquifer where water supply wells may eventually be adversely impacted by landfill leachate.

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REFERENCES

- Cherry, J.A., 1983. Occurrence and migration of contaminants in groundwater at municipal landfills on sand aquifers. In: Environment and Solid Wastes. Editors, C.W. Francis, S.I. Auerbach and V.A. Jacobs, Butterworths, Boston, p. 127-147.
- Cherry, J.A., 1983. Migration of contaminants in groundwater at a landfill: A case study. *Journal of Hydrology*, Vol. 63, no. 1-2, May 1983.
- Cherry, J.A., Barker, J.F., Buszka, P.M., Hewetson, J.P. and Mayfield, C.I., 1981. Contaminant occurrence in an unconfined sand aquifer at a municipal landfill. *Proc. Fourth Annual Madison Conference of Applied Research and Practice of Municipal and Industrial Waste*, Sept. 28-30, Madison, Wisconsin, pp. 393-411.
- Cherry, J.A., Gillham, R.W., Anderson, E.G. and Johnson, P.E., 1983. Migration of contaminants in groundwater at a landfill: A case study. 2. Groundwater monitoring devices, *Journal of Hydrology*, Vol. 63, pp. 31-49.

Cherry, J.A. and Johnson, P.E., 1982. A multilevel device for hydraulic head monitoring and groundwater sampling in fractured rock, *Ground Water Monitoring Review*, Vol. 2, no. 3, pp. 42-44.

Cherry, J.A., Johnson, P.E., Blackport, R.J. and Hewetson, J.P., 1984. Development and application of a multilevel device for groundwater monitoring in fractured rock. *Canadian Geotechnical Journal* (in press).

Hokkanen, G.E.. Application of the alternating direction Galerkin technique to the simulation of contaminant transport at the Borden landfill. M.Sc. Thesis, University of Waterloo, 1984.

King, K.S., 1983. Carbon isotope geochemistry of a landfill leachate. Unpublished M.Sc. Thesis, University of Waterloo, 120 p.

Kobayashi, H. and Rittman, B.E., 1982. Microbial removal of hazardous organic compounds. *Environ. Sci. Technol.*, 16, p. 171A-181A.

MacFarlane, D.S., Cherry, J.A., Gillham, R.W. and Sudicky, E.A., 1983. Migration of contaminants in groundwater at a landfill: a case study. 1. Groundwater flow and plume delineation.

Nicholson, R.V., Cherry, J.A. and Reardon, E.J., 1983. Migration of contaminants in groundwater at a landfill: a case study. 6. Hydrochemical patterns and processes. *Journal of Hydrology*, Vol. 63, p. 131-176.

Pankow, J.F., Isabelle, L.M., Hewetson, J.P. and Cherry, J.A., 1984a. A tube and cartridge method for down-hole sampling for trace organics in groundwater. *Ground Water* (submitted in October, 1984).

Pankow, J.F., Isabelle, L.M., Hewetson, J.P. and Cherry, J.A., 1984b. A syringe and cartridge method for down-hole sampling for trace organics in groundwater. *Ground Water* Vol. 22, no. 3, pp. 330-339.

Reinhard, M., Goodman, N.L. and Barker, J.F., 1984. Occurrence and distribution of organic chemicals in two landfill leachate plumes. *Environ. Sci. Technol.*, (accepted for Nov. 1984).

Reinhard, M., Graydon, J.W., Goodman, N.L. and Barker, J.F., 1984a. The distribution of selected trace organics in the leachate plume of a municipal landfill. *Proc. 2nd Internat. Conf. Ground-Water Quality Res.*, Tulsa, OK, March 27, 1984.